Effect of Microstructure on Li Storage Performance in Dispersed Metal Composite Anodes

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Dispersed metal alloys have recently been studied as negative electrodes for Li-ion batteries due to their high gravimetric and volumetric capacity.[1-5] It is now generally believed that fine metal particles tolerate cycling induced volume change better than do coarse particles or bulk metals. However, the critical particle size necessary to prevent mechanical failure during cycling for various systems still needs to be established. In addition, cost effective processing methods need to be developed if this class of electrode is to be widely used.

We have developed an approach based on the partial reduction of mixed oxides was used to produce metal-oxide composites of various size scale and microstructures.[6,7] In the present work, Sb was used as the model metal system and $Mn_2Sb_2O_7$ fluorite as the starting metal oxide. Experimental observations of various cycled samples by x-ray and scanning electron microscopy (STEM) indicate that the Sb metal crystallite size is reduced upon cycling to the 5-50 nm range. These observations suggest that there exists a critical Sb metal particle size for stable cycling that is in this range.

Subsequently, the partial reduction reaction was controlled such that internal reduction is achieved resulting in finer metal dispersions. This is because coarsening of internal metal particles is prohibited by the ceramic matrix. Figure 1 shows an example (backscattering scanning electron micrograph) of a partially reduced $Mn_2Sb_2O_7$, showing internally reduced Sb metal embedded in an MnO matrix. It was found that materials consisting of internal metal precipitates exhibit superior cycling performance to those with externally metal particles. Figure 2 shows a transmission electron microscope (TEM) image of a cycled Sb-MnO composite, where it is seen that Sb particles of 10-30 nm particle size remain embedded in an MnO matrix, the composite particle having survived repeated cycling. The corresponding electrochemical cycling data is shown in Fig. 3. Although fading was observed after the 20th cycle, when the cell was reassembled, the capacity was recovered. This suggests that the mechanism of failure is, therefore, not based on the material alone. Understanding of the failure mechanism and optimization of the composite microstructure will be discussed in the talk.

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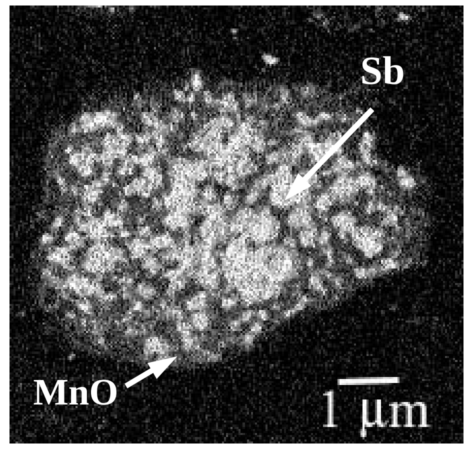

Figure 1. Internal Sb embedded in MnO matrix obtained by partially reducing $Mn_2Sb_2O_7$ (425°C, H_2)

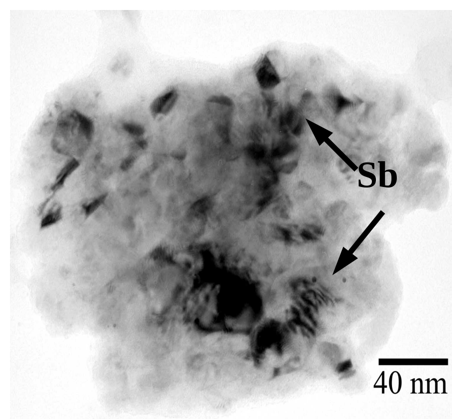

Figure 2. Cycled Sb-MnO nanocomposite particle formed by the partial reduction.

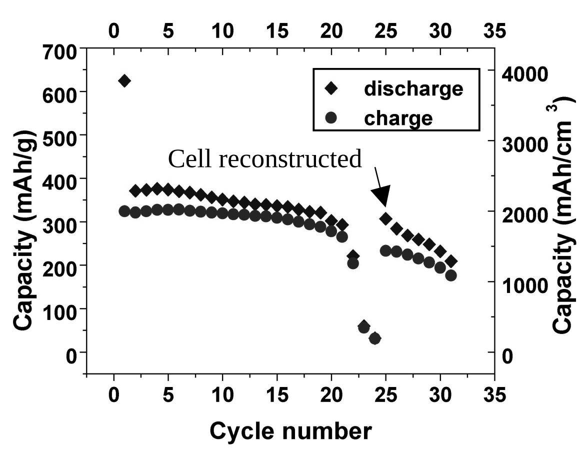

Figure 3. Electrochemical cycling of partially reduced $Mn_2Sb_2O_7$ shown in Fig 2.